DESCRIPTION

POLYAMIDE RESIN COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to such a polyamide resin composition that is suitably used as a material of a gasoline tank and a material of a molded article, such as a hollow molded container including a beverage bottle, a film and a sheet. It also relates to such a polyamide resin composition that is good in heat stability upon molding, is excellent in color tone, suffers less increase in filter back pressure, and is excellent in productivity.

BACKGROUND ART

[0002]

Polyamide is being widely used in such purposes as a hollow molded container, a film, a sheet wrapping material, engineering plastics and fibers owing to the excellent physical and mechanical characteristics thereof. Representative examples thereof include an aliphatic polyamide, such as

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nylon 66, and in addition, a number of kinds of polyamide have been known that use an aromatic diamine, such as p-xylylenediamine (PXDA) and m-xylylenediamine (MXDA), as a starting material to realize reduction in water absorptivity and improvement in elastic modulus.

[0003]

Polyamide is relatively unstable to heat as compared to polyester and the like, and sometimes suffers gelation, yellowing and the like due to heat deterioration and thermal oxidation deterioration.

[0004]

As a measure for suppressing polyamide from suffering heat deterioration, such a method is proposed that a phosphonic acid compound or a phosphorous acid compound, and an alkali metal are added to polyamide (see, for example, Patent Document 1).

[0005]

As a measure for suppressing polyamide from suffering heat deterioration, such a method is proposed that a phosphinic acid compound, a phsophrous acid compound or a phosphonic acid compound, and an alkali metal are added to polyamide, and phenylenediamine and/or a derivative thereof is

added to polyamide in an amount of from 0.01 to 2% by weight (see, for example, Patent Document 2).

[0006]

As a measure for preventing polyamide from suffering heat deterioration at a melting point thereof or lower in a system having no oxygen present therein, such a method is proposed that a pyrophosphite salt, an amide compound of an organic phosphinic acid, a barium salt of a monoester or diester of phosphorous acid, a copper salt of a monoester or diester of orthophosphoric acid, or the like is added (see, for example, Patent Documents 3, 4, 5 and 6).

[0007]

As a measure for preventing a gelled product of polyamide formed from m-xylylenediamine and adipic acid from occurring, it is considered that at least one kind selected from a lubricant, an organic phosphorous stabilizer, a hindered phenol compound and a hindered amine compound is added in an amount of from 0.0005 to 0.5 part by weight (see, for example, Patent Document 7).

These measures exert effect for preventing gelation due to a network structure with a three-dimensional structure in polyamide, but a finer

filter is being used on molding a resin for purposes requiring increased precision in recent years, which brings about such a problem that a filter is often clogged, and thus is necessarily exchanged frequently.

Patent Document 1:   JP-A-49-45960

Patent Document 2:   JP-A-49-53945

Patent Document 3:   JP-A-45-11836

Patent Document 4:   JP-A-45-35667

Patent Document 5:   JP-A-45-12986

Patent Document 6:   JP-A-46-38351

Patent Document 7:   JP-A-2001-164109

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008]

The invention relates to such a polyamide resin composition that is suitably used as a material of a gasoline tank and a material of a molded article, such as a hollow molded container including a beverage bottle, a film and a sheet. It is also to provide a polyamide resin composition that is suppressed in filter clogging and is hard to suffer yellowing due to heat deterioration on polymerization and molding by containing such a polyamide resin that is good in heat stability upon

polymerization and molding, is excellent in color tone with less degree of yellowing, suffers less increase in filter back pressure, and is excellent in productivity.

MEANS FOR SOLVING THE INVENTION

[0009]

1. A polyamide resin composition containing mainly m-xylylenediamine (MXDA) as a diamine component and mainly adipic acid (AA) as a dicarboxylic acid component, wherein the polyamide resin composition has a back pressure increasing coefficient K* satisfying the following equation (1):

$$0 < K* < 15 \qquad\qquad (1)$$

wherein K* represents a back pressure increasing coefficient expressed by the following equation:

$$K* = [\Delta P \ (MPa)/T \ (hr)]/[Q \ (kg/hr)/S \ (cm^2)]$$

wherein ΔP (MPa) represents a difference between an initial secondary pressure of a gear pump and a secondary pressure thereof after a lapse of T (hr);

T (hr) represents a period of time of filtering the polyamide resin composition with a filter; Q (kg/hr) represents a discharge amount of the polyamide resin composition; S (cm^2) represents a filtering area of the filter; and the filter has a filtering diameter of 20 μm.

[0010]

2.   The polyamide resin composition described in the item 1, wherein the polyamide resin composition has a back pressure increasing coefficient K* satisfying the following equation (2):

$$0 < K* < 5 \qquad\qquad (2)$$

wherein K* represents a back pressure increasing coefficient expressed by the following equation:

$$K* = [\Delta P \ (MPa)/T \ (hr)]/[Q \ (kg/hr)/S \ (cm^2)]$$

wherein ΔP (MPa) represents a difference between an initial secondary pressure of a gear pump and a secondary pressure thereof after a lapse of T (hr); T (hr) represents a period of time of filtering the polyamide resin composition with a filter; Q (kg/hr)

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represents a discharge amount of the polyamide resin composition; S (cm^2) represents a filtering area of the filter; and the filter has a filtering diameter of 20 μm.

[0011]

3.   A polyamide resin composition containing mainly m-xylylenediamine (MXDA) as a diamine component and mainly adipic acid (AA) as a dicarboxylic acid component, the polyamide resin composition having contents of phosphorous atoms (P) and sodium atoms (Na) satisfying the following equations (3) and (4):

$$30 \leq P < 200 \text{ ppm} \qquad (3)$$
$$3.0 < Na/P \text{ (molar ratio)} < 7.0 \qquad (4)$$

[0012]

4.   The polyamide resin composition as described in the item 3, wherein the polyamide resin composition has a Co-b value satisfying the following equation (5):

$$-3 < Co-b < 10 \qquad (5)$$

[0013]

5.   A polyamide resin composition containing mainly m-xylylenediamine (MXDA) as a diamine component and mainly adipic acid (AA) as a dicarboxylic acid component, the polyamide resin composition having contents of phosphorous atoms (P) and an alkali metal (M) satisfying the following equations (6) and (7):

$$0 \leq P < 30 \text{ ppm} \qquad (6)$$
$$0.1 \leq M < 45 \text{ ppm} \qquad (7)$$

wherein M represents an alkali metal species, such as Na, Li and K.

[0014]

6.   The polyamide resin composition as described in the item 5, wherein the polyamide resin composition has a Co-b value satisfying the following equation (8):

$$3 < Co\text{-}b < 10 \qquad (8)$$

ADVANTAGE OF THE INVENTION

[0015]

The polyamide resin composition of the invention is good in heat stability upon molding, is

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excellent in color tone, and suffers less increase in filter back pressure. The invention is suitably used as a material of a gasoline tank and a material of a molded article, such as a hollow molded container including a beverage bottle, a film and a sheet, and can produce it with high productivity.

BEST MODE FOR CARRYING OUT THE INVENTION
[0016]

Embodiments of the polyamide resin composition of the invention will be described in detail.

As the dicarboxylic acid component of the polyamide resin composition used in the invention, adipic acid is mainly used, and in addition, one kind or two or more kinds of an aliphatic dicarboxylic acid, such as sebacic acid, suberic acid, azelaic acid, undecanoic acid, undecanedioic acid and dimer acid, and an aromatic dicarboxylic acid, such as terephthalic acid, isophthalic acid, orthophthalic acid, xylylenedicarboxylic acid and naphthalenedicarboxylic acid, may be used in an arbitrary proportion.
[0017]

A polyamide resin contained in the polyamide resin composition of the invention contains mainly

adipic acid as a dicarboxylic acid component, and preferably contains in an amount of 80% by mole or more, more preferably 90% by mole or more, and further preferably 95% by mole or more.

[0018]

As the diamine component of the polyamide resin composition, m-xylylenediamine is mainly used, and in addition, an aliphatic diamine compound, such as ethylenediamine, 1-methylethylenediamine, 1,3-propylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, undecamethylenediamine and dodecamethylenediamine, an alicyclic diamine compound, such as cyclohexanediamine and bis-(4,4'-aminohexyl)methane, and an aromatic diamine compound, such as p-xylylenediamine and p-bis-(2-aminoethyl)benzene, may be used.

One kind or two or more kinds of the diamine may be used in an arbitrary proportion.

[0019]

The polyamide resin contained in the polyamide resin composition of the invention contains mainly m-xylylenediamine as a diamine component, and

preferably contains in an amount of 80% by mole or more, more preferably 90% by mole or more, and further preferably 95% by mole or more.
[0020]

In addition to the aforementioned diamine and dicarboxylic acid, a lactam compound, such as ε-caprolactam and laurolactam, an aminocarboxylic acid compound, such as aminocaproic acid and aminoundecanoic acid, an aromatic aminocarboxylic acid, such as p-aminomethylbenzoic acid, and the like may be used as a copolymerization component. Among these, ε-caprolactam is preferably used.
[0021]

Examples of a polymer capable of being contained in the polyamide resin composition of the invention include a homopolymer, such as poly-m-xylyleneadipamide, a m-xylylenediamine/adipic acid/isophthalic acid copolymer, and a m-xylylene/p-xylyleneadipamide copolymer.
[0022]

In order to obtain a polyamide resin composition of the invention having a low back pressure coefficient K* and good color tone, the contents of metals and the like in the polyamide resin composition are preferably that phosphorous

atoms (P) and sodium atoms (Na) satisfy the ranges
of the following equations (3) and (4) (embodiment
A):

$$30 \leq P < 200 \text{ ppm} \qquad (3)$$
(ppm: amount (mg) per 1 kg of polymer)
$$3.0 < Na/P \text{ (molar ratio)} < 7.0 \qquad (4)$$

[0023]

The lower limit of the content of phosphorous
atoms (P) in the embodiment A is more preferably 40
ppm or more, further preferably 50 ppm or more,
particularly preferably 60 ppm or more, and most
preferably 70 ppm or more. The upper limit thereof
is preferably 170 ppm or less, more preferably 160
ppm or less, further preferably 150 ppm or less, and
particularly preferably 130 ppm or less. In the case
where the content of phosphorous atoms is too small,
the heat stability may be lowered, and the color
tone of the polymer may be deteriorated. In the case
where the content of phosphorous atoms is too large,
on the other hand, the raw material cost for the
additive is increased to cause increase in
production cost, and the filter is often clogged

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with foreign matter, which brings about such a possibility that the productivity is deteriorated.

[0024]

The lower limit of the Na/P molar ratio is more preferably 3.5 or more, further preferably 4.0 or more, and particularly preferably 4.5 or more. The upper limit thereof is more preferably 6.5 or less, further preferably 6.0 or less, and still further preferably 5.5 or less. In the case where Na/P molar ratio is too small, the viscosity is considerably increased, such a risk is increased that gelled products are mixed in upon molding, and the back pressure upon melt filtering may be increased. In the case where the Na/P molar ratio is too large, on the other hand, the polymerization reaction rate may be decreased severely, and the productivity may be deteriorated.

[0025]

There are such cases that alkali metals are avoided for applying to an electronic material or the like, and slight bleed out of a phosphorous compound to the surface is avoided. In these cases, as one embodiment of the invention, the contents of phosphorous atoms (P) and an alkali metal (M) of the

polyamide of the invention preferably satisfy the
following equations (6) and (7) (embodiment B):

$$0 \leq P < 30 \text{ ppm} \tag{6}$$

(ppm: amount (mg) per 1 kg of polymer)

$$0.1 \leq M < 45 \text{ ppm} \tag{7}$$

wherein M represents an alkali metal species, such
as Na, Li and K.

[0026]

The lower limit of the content of phosphorous
atoms (P) in the embodiment B is more preferably 1
ppm or more, further preferably 3 ppm or more, and
particularly preferably 5 ppm or more. The upper
limit thereof is preferably 25 ppm or less, more
preferably 20 ppm or less, further preferably 15 ppm
or less, particularly preferably 12 ppm or less, and
most preferably 9 ppm or less. The lower limit of
the content of an alkali metal (M) is more
preferably 1 ppm or more, further preferably 3 ppm
or more, and particularly preferably 5 ppm or more.
The upper limit thereof is preferably 40 ppm or less,
more preferably 35 ppm or less, further preferably
30 ppm or less, still further preferably 25 ppm or
less, yet further preferably 20 ppm or less,

particularly preferably 15 ppm or less, and still particularly preferably 10 ppm or less. In the production process, the number of cleaning operation of a reaction vessel may be increased, ion exchange of water in a cooling step should be sufficiently carried out, and ion exchanged water or distilled water should be used as water for dissolving the raw materials, which bring about considerable increase in cost. In the case where the content of phosphorous atoms or an alkali atom is too large, the raw material cost for the additive is increased to cause increase in production cost, and the frequency of filter clogging with the additive upon filtering is increased, which may bring about deterioration in productivity.
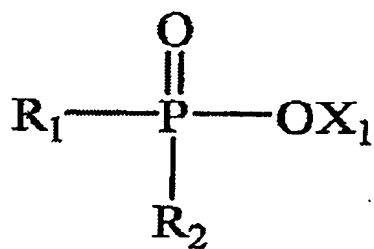
[0027]

The content ratio between the phosphorous compound and the alkali metal compound may be an arbitrary value as far as the contents of them are within the ranges defined in the invention.
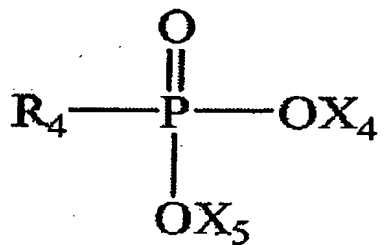
[0028]

Examples of the compound containing a phosphorous atom in the polyamide resin composition used in the invention include compounds represented by the following chemical formulae (C-1) to (C-4).
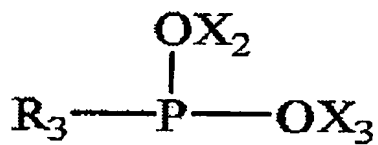
[0029]

$$R_1 - \underset{\underset{R_2}{|}}{\overset{\overset{O}{\|}}{P}} - OX_1$$

(C-1)

[0030]

$$R_4 - \underset{\underset{OX_5}{|}}{\overset{\overset{O}{\|}}{P}} - OX_4$$

(C-2)

[0031]

$$R_3 - \underset{\underset{}{\overset{OX_2}{|}}}{P} - OX_3$$

(C-3)

[0032]

$$R_5O - \underset{\underset{}{\overset{OR_6}{|}}}{P} - OR_7$$

(C-4)

[0033]

wherein R_1 to R_7 each represents a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group or an arylalkyl group; and X_1 to X_5 each represents a hydrogen atom, an alkyl group, an aryl group, a cycloalkyl group, an arylalkyl group or an alkali metal, provided that one of R_1 to R_7 and one of X_1 to X_5 may be bonded to form a cyclic structure.
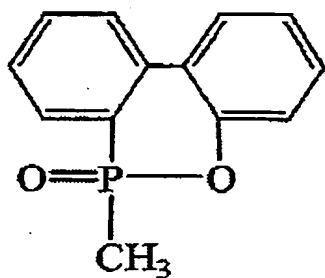
[0034]

Examples of a phosphinic acid compound represented by the chemical formula (C-1) include dimethylphosphinic acid, phenylmethylphosphinic acid, hypophosphorous acid, sodium hypophosphite, ethyl hypophosphite, the following compounds:

[0035]

and

[0036]

$$O=P-O$$

CH₃

represented by the structure:

O=P—O
|
CH₃

,
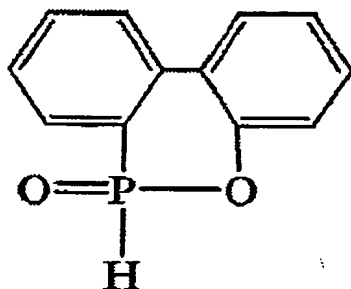
a hydrolyzed product thereof, and a condensate of
the phosphinic acid compound.

[0037]

Examples of a phosphonous acid compound
represented by the chemical formula (C-2) include
phenylphosphonous acid, sodium phenylphosphonite and
ethyl phenylphosphonite.

Examples of a phosphonic acid compound
represented by the chemical formula (C-3) include
phenylphosphonic acid, ethylphosphonic acid, sodium
phenylphosphonate, diethyl phenylphosphonate and
sodium ethylphosphonate.

Examples of a phosphorous acid compound
represented by the chemical formula (C-4) include
phosphorous acid, sodium hydrogenphosphite, sodium
phosphite, triethyl phosphite, triphenyl phosphite
and pyrophosphorous acid.

[0038]

Examples of a sodium metallic compound capable of being used in the polyamide resin composition of the invention include sodium hydroxide, sodium acetate, sodium acetate, sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide and sodium carbonate, and among these, sodium hydroxide and sodium acetate are preferably used, but the invention is not limited to these compounds.
[0039]

Examples of the alkali metal include lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, lithium acetate, sodium acetate, potassium acetate, rubidium acetate, cesium acetate, sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide, potassium methoxide, lithium methoxide and sodium carbonate, but the invention is not limited to these compounds.
[0040]

In order to mix the phosphorous atom-containing compound in the polyamide resin composition of the invention, it may be added to a raw material before polymerization of polyamide or during polymerization, or may be melt-mixed with the polymer. In order to prevent polyamide from suffering heat deterioration

upon solid phase polymerization, it is preferred
that the phosphorous atom-containing compound is
added before starting polymerization.

[0041]

The color b (Co-b) value upon molding the
polyamide resin composition of the invention to
chips preferably satisfies the following equation
(5):

$$-3 < Co\text{-}b < 10 \qquad\qquad (5)$$

[0042]

The upper limit of the Co-b value in the
embodiment A is preferably 5, more preferably 4,
further preferably 3, and particularly preferably 2.
In the case where the Co-b value is too high,
yellowing occurring on a post-process of a bottle, a
film, fibers or the like is outstanding, which may
brings about deterioration in quality of products.
In the case where the Co-b value is decreased
excessively, the addition amount of a stabilizer,
such as a phosphorous atom-containing compound, may
be too large, whereby it is disadvantageous in cost,
and filter clogging may occur due to the additive.
In order to make the Co-b value within the

aforementioned range, the addition amounts of the phosphorous atom-containing compound and the sodium metallic compound may be optimized, and furthermore such measures may be employed that the upper limit of the temperature on reaction is 270°C or less, preferably 265°C or less, and more preferably 260°C or less, and the oxygen concentration on reaction is preferably 200 ppm or less, preferably 150 ppm or less, and further preferably 100 ppm or less.

[0043]

While there are cases where certain coloration is observed in the embodiment B, the color b (Co-b) value upon molding the polyamide resin composition of the invention to chips preferably satisfies the following equation (8):

$$3 < Co\text{-}b < 10 \tag{8}$$

[0044]

The upper limit of the Co-b value is preferably 9, more preferably 8, further preferably 7, and particularly preferably 5. In the case where the Co-b value is decreased excessively, the addition amount of a stabilizer, such as a phosphorous atom-containing compound, may be too large, whereby it is

disadvantageous in cost, and filter clogging may occur due to the additive. In the case where the Co-b value is too high, yellowing occurring on a post-process of a bottle, a film, fibers or the like is outstanding, which may brings about deterioration in appearance performance of products. In the case where color b value is 5 or more and less than 10, a molded article has slightly yellowish appearance and has slightly yellowish appearance. Therefore, it is difficult to use as a molded article for a purpose that is not allowed to have yellowish appearance (such as products having white to blue appearance), but may be used without problem as a molded article for a purpose that prefers yellowish appearance or that is allowed to have yellowish appearance (such as products having yellow to black appearance and products with no requirement in appearance performance), which provides industrial significance.

[0045]

The polyamide resin composition of the invention can be produced by a method of reacting an aqueous solution of an aminocarboxylate salt formed from a diamine and a dicarboxylic acid by heating under increased pressure or ordinary pressure, or a method of directly reacting a diamine and a

dicarboxylic acid by heating under ordinary pressure.
Chips of the polyamide obtained through the melt-
polycondensation reaction may be subjected to solid
phase polymerization to obtain a polyamide resin
composition having a higher viscosity.
[0046]

The polycondensation reaction of the polyamide
resin composition may be carried out with a batch
reaction apparatus or a continuous reaction
apparatus.
[0047]

The polyamide resin composition of the
invention preferably has a back pressure increasing
coefficient K* satisfying the following equation
(1):

$$0 < K* < 15 \tag{1}$$

wherein K* represents a back pressure increasing
coefficient expressed by the following equation:

$$K* = [\Delta P \ (MPa)/T \ (hr)]/[Q \ (kg/hr)/S \ (cm^2)]$$

wherein the filter has a filtering diameter of 20 μm.

The polyamide resin composition is fused by using a uniaxial extruder (heater temperature: 285°C, average residence time: 10 minutes) and extruded in a given amount at a rate of from 3 to 6 g/min by using a gear pump. Foreign matters in the polymer are filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump is recorded with lapse of time. The difference in pressure after extruding for 4 hours is applied to the following equation to obtain the back pressure increasing value K*.

$$K* = [\Delta P \ (MPa)/T \ (hr)]/[Q \ (kg/hr)/S \ (cm^2)]$$

ΔP (MPa): (secondary pressure of gear pump after 4 hours) − (initial pressure)

T (hr): period of time of filtering the polyamide resin composition with the filter (4 hours)

Q (kg/hr): discharge amount of the polyamide resin composition (3 to 6 g/min)

S (cm^2): filtering area of the filter (1.538 cm^2)

[0048]

The back pressure increasing value K* is preferably 10 or less, more preferably 8 or less, further preferably 7 or less, still further

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preferably 6 or less, and particularly preferably less than 5.

[0049]

The lower limit of the back pressure increasing coefficient K* is preferably lowered to such a value that is equal to K* when no additive is mixed, and the K* value with no additive may be practically considered as one reference of the lower limit. The lower limit of K* is not particularly limited, and is 1 in one embodiment, 1.5 in another embodiment, 2 in still another embodiment, and 2.5 in a further embodiment.

[0050]

In the case where the back pressure increasing coefficient K* is too high, the frequency of occurrence of clogging may be increased in a post-process requiring filtration with a filter, such as molding of a bottle and formation of a film, and there arises a high possibility of increase in cost due to deterioration in productivity.

In the case where K* is 5 or more and less than 15, slight filter clogging is observed but is not a level causing a practical problem, and the objects of the invention can be sufficiently attained. In the case where continuous production is carried out

for a considerably long period of time, however, there may be a possibility of causing increased clogging, and thus K* is preferably less than 5 when continuous production is carried out for a considerably long period of time.

[0051]

The back pressure increasing rate K* is more preferably 4 or less, further preferably 3.5 or less, and particularly preferably 3 or less. In the case where K* is too large, the frequency of occurrence of clogging may be increased in a post-process requiring filtration with a filter, such as molding of a bottle and formation of a film, and there arises a high possibility of increase in cost due to deterioration in productivity.

[0052]

The lower limit of the back pressure increasing coefficient K* is preferably lowered to such a value that is equal to K* when no additive is mixed even in this case, and the K* value with no additive may be practically considered as one reference of the lower limit. The lower limit of K* is not particularly limited, and is 1 in one embodiment, 1.5 in another embodiment, 2 in still another embodiment, and 2.5 in a further embodiment.

EXAMPLES

[0053]

The invention will be illustrated with reference to the following Examples, but the invention shall not be construed as being limited to the examples. The measuring methods of the main characteristic values in the specification will be described below.

[0054]

(1)   Relative Viscosity of Polyamide Resin Composition (RV)

0.25 g of a specimen was dissolved in 25 mL of 96% sulfuric acid, and 10 mL of the resulting solution was measured with an Ostwald viscometer at 20°C to obtain RV by the following equation.

$$RV = t/t_0$$

t_0:   number of seconds of dropping solvent

t: number of seconds of dropping specimen solution

[0055]

(2)   Color b of Polyamide Resin Composition

Color b was measured by using Model 100DP, produced by Nippon Denshoku Industries Co., Ltd. In

the measurement method, chips were placed in a glass cell to a level of eight out of ten. After lightly shaking the cell to stuff densely, the resin was added until a lid could be closed, and then the lid was closed. The cell filled with the chips was placed on a sample stage and measured. Upon measurement, the chips were replaced and stuffed by every measurement. The measurement was carried out three times, and an average thereof was obtained.

[0056]

(3)   Analysis of P

A specimen was subjected to dry ashing decomposition by allowing to stand with sodium carbonate or to wet decomposition in a sulfuric acid-nitric acid-perchloric acid system or a sulfuric acid-perchloric acid system, to convert phosphorous to orthophosphoric acid. A molybdate salt was reacted therewith in a 1 mol/L sulfuric acid solution to form phosphomolybdic acid, which was reduced with hydrazine sulfate to form heteropoly blue. The absorbance of the heteropoly blue at 830 nm was measured with an absorptiometer (UV-150-02, produced by Shimadzu Corp.) for colorimetric determination.

[0057]

(4)   Analysis of Na and Li

A specimen was subjected to ashing decomposition in a platinum crucible, to which 6 mol/L hydrochloric acid was added, followed by subjecting to evaporation to dryness. The residue was dissolved with 1.2 mol/L hydrochloric acid, and the solution was subjected to quantitative determination by atomic absorption (AA-640-12, produced by Shimadzu Corp.).

[0058]

(5)   Back Pressure Increasing Test

A polyamide resin composition was fused by using a uniaxial extruder (heater temperature: 285°C, average residence time: 10 minutes) and extruded in a given amount at a rate of from 3 to 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The difference in pressure after extruding for 4 hours was applied to the following equation to obtain a back pressure increasing value K*.

[0059]

$$K^* = [\Delta P \text{ (MPa)}/T \text{ (hr)}]/[Q \text{ (kg/hr)}/S \text{ (cm}^2)]$$

ΔP (MPa): (secondary pressure of gear pump after 4 hours) - (initial pressure)

T (hr): period of time of filtering the polyamide resin composition with the filter (4 hours)

Q (kg/hr): discharge amount of the polyamide resin composition (3 to 6 g/min)

S (cm^2): filtering area of the filter (8.166 cm^2)

[0060]

m-Xylylene group-containing polyamide (MXD6) used in Examples and Comparative Examples, and Copolymers thereof

[0061]

EXAMPLE A-1

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine and 29.65 kg of adipic acid, which had been precisely weighed, were mixed at an inter temperature of 85°C to obtain a transparent solution. 1.37 g of $NaH_2PO_2 \cdot H_2O$ and 3.71 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring

in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was removed outside the system, at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin was then solidified by cooling and cut with a strand cutter to obtain chips. The resulting resin had a relative viscosity (RV) of 2.10 and a Co-b value of 3.3. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, and then cooled to obtain resin chips. The chips had a water content of 200 ppm and residual amounts of phosphorous atoms and sodium atoms were P = 40 ppm and Na = 134 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering

diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 2.5. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0062]

EXAMPLE A-2

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 1.71 g of $NaH_2PO_2 \cdot H_2O$ and 3.97 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.23 and a Co-b value of 3.1. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, and then cooled to obtain chips. The chips had a water content of 250 ppm and residual amounts of phosphorous atoms and sodium atoms were P = 50 ppm and Na = 148 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the

polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 3.5. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0063]

EXAMPLE A-3

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 3.42 g of $NaH_2PO_2 \cdot H_2O$ and 6.62 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of -0.8. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was -1.1, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 100 ppm

and Na = 260 ppm, respectively. The polyamide resin
composition was fused by using a uniaxial extruder
and extruded in a given amount at a rate of 3 g/min
by using a gear pump. Foreign matters in the polymer
were filtered with a filter having a filtering
diameter of 20 μm, and the pressure on the secondary
side of the gear pump was recorded with lapse of
time. The back pressure increasing coefficient K*
after extruding for 4 hours was 14. Observation of
the filter revealed that slight clogging was found
but was in a level causing no practical problem.
Observation of the heat deterioration state of the
resulting extrusion·molded article revealed that no
gelled product due to heat deterioration was
observed.

[0064]

EXAMPLE A-4

The polymerization method of polyamide was
carried out in the same manner as in Example A-1
except that 3.42 g of $NaH_2PO_2 \cdot H_2O$ and 7.95 g of
CH_3COONa as additives were added. The resulting
resin had a relative viscosity (RV) of 2.10 and a
Co-b value of -0.9. The resulting resin was dried in
a 100 L blender at an inner temperature of 120°C for
12 hours, further subjected to solid phase

polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was -1.3, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 100 ppm and Na = 297 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 7.8. Observation of the filter revealed that slight clogging was found but was in a level causing no practical problem. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0065]

EXAMPLE A-5

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 3.42 g of $NaH_2PO_2 \cdot H_2O$ and 10.59 g of

CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.12 and a Co-b value of 1.0. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours. The residual amounts of phosphorous atoms and sodium atoms were P = 100 ppm and Na = 371 ppm, respectively, in this stage. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 3.7. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0066]

EXAMPLE A-6

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 3.42 g of $NaH_2PO_2 \cdot H_2O$ and 0.59 g of

CH$_3$COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.12 and a Co-b value of 1.0. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was 2.0, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 100 ppm and Na = 371 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 4.5. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0067]

EXAMPLE A-7

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 5.13 g of $NaH_2PO_2 \cdot H_2O$ and 15.89 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of -0.8. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.50, the Co-b value was 1.5, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 150 ppm and Na = 557 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 5.2. Observation of the filter revealed that slight clogging was found but was in a level causing no practical problem.

Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0068]

EXAMPLE A-8

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 6.50 g of $NaH_2PO_2 \cdot H_2O$ and 25.16 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 3.5. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.10, the Co-b value was 2.5, and the water content was 250 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 190 ppm and Na = 846 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary

side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K^* after extruding for 4 hours was 4.0. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0069]

EXAMPLE A-9

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine, 26.41 kg of adipic acid and 3.34 kg of terephthalic acid, which had been precisely weighed, were mixed at an inter temperature of 100°C to obtain a transparent solution. 5.13 g of $NaH_2PO_2 \cdot H_2O$ and 13.91 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was removed outside the system,

at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin was then solidified by cooling and cut with a strand cutter to obtain resin chips. The resulting resin had a relative viscosity (RV) of 2.35 and a Co-b value of 4.9. The residual amounts of phosphorous atoms and sodium atoms were P = 150 ppm and Na = 501 ppm, respectively. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, and then cooled to obtain chips. The RV was 2.35, the Co-b value was 4.9, and the water content was 250 ppm, in this stage. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was

recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 14. Observation of the filter revealed that slight clogging was found but was in a level causing no practical problem. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0070]

EXAMPLE A-10

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine, 26.41 kg of adipic acid and 3.45 kg of cyclohexanedicarboxylic acid, which had been precisely weighed, were mixed at an inter temperature of 100°C to obtain a transparent solution. 5.13 g of $NaH_2PO_2 \cdot H_2O$ and 13.91 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was

removed outside the system, at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin was then solidified by cooling and cut with a strand cutter to obtain resin chips. The resulting resin had a relative viscosity (RV) of 2.3 and a Co-b value of -3.1. The residual amounts of phosphorous atoms and sodium atoms were P = 150 ppm and Na = 501 ppm, respectively. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, and then cooled to obtain chips. The RV was 2.30, the Co-b value was -2.3, and the water content was 250 ppm, in this stage. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the

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secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 12. Observation of the filter revealed that slight clogging was found but was in a level causing no practical problem. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0071]

EXAMPLE B-1

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine and 29.65 kg of adipic acid, which had been precisely weighed, were mixed at an inter temperature of 85°C to obtain a transparent solution. 0.07 g of $NaH_2PO_2 \cdot H_2O$ and 0.17 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was

removed outside the system, at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin was then solidified by cooling and cut with a strand cutter to obtain resin chips. The resulting resin had a relative viscosity (RV) of 2.10 and a Co-b value of 5.5. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was 6.5, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 1 ppm and Na = 1 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer

were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 3.0. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0072]

EXAMPLE B-2

The polymerization method of polyamide was carried out in the same manner as in Example B-1. Sodium from water used in a cooling step was intentionally made remain in the resin, and the effect of sodium as an additive was evaluated. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 7.8. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was 7.8, and the water content was 200 ppm, in this stage. The residual amounts of

phosphorous atoms and sodium atoms were P = 0 ppm and Na = 0.1 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 2.2. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0073]

EXAMPLE B-3

The polymerization method of polyamide was carried out in the same manner as in Example B-1 except that 0.33 g of $NaH_2PO_2 \cdot H_2O$ and 0.86 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 5.6. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase

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polymerization at an inner temperature of 180°C, and
then cooled to obtain chips. The RV was 2.65, the
Co-b value was 6.2, and the water content was 200
ppm, in this stage. The residual amounts of
phosphorous atoms and sodium atoms were P = 5 ppm
and Na = 5 ppm, respectively. The polyamide resin
composition was fused by using a uniaxial extruder
and extruded in a given amount at a rate of 3 g/min
by using a gear pump. Foreign matters in the polymer
were filtered with a filter having a filtering
diameter of 20 μm, and the pressure on the secondary
side of the gear pump was recorded with lapse of
time. The back pressure increasing coefficient K*
after extruding for 4 hours was 3.9. Observation of
the filter revealed that no clogging was found.
Observation of the heat deterioration state of the
resulting extrusion molded article revealed that no
gelled product due to heat deterioration was
observed.

[0074]

EXAMPLE B-4

The polymerization method of polyamide was
carried out in the same manner as in Example B-1
except that 1.54 g of $NaH_2PO_2 \cdot H_2O$ and 0.59 g of
CH_3COONa as additives were added. The resulting

resin had a relative viscosity (RV) of 2.15 and a Co-b value of 5.3. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, and then cooled to obtain chips. The water content was 200 ppm in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 9 ppm and Na = 9 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 6 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 4.6. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0075]

EXAMPLE B-5

The polymerization method of polyamide was carried out in the same manner as in Example B-1 except that 2.6 g of $NaH_2PO_2 \cdot H_2O$ and 0.9 g of CH_3COONa

as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 3.5. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was 3.6, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 15 ppm and Na = 15 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 3.7. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0076]

EXAMPLE B-6

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine, 26.41 kg of adipic acid and 3.34 kg of terephthalic acid, which had been precisely weighed, were mixed at an inter temperature of 100°C to obtain a transparent solution. 1.54 g of $NaH_2PO_2 \cdot H_2O$ and 0.8 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was removed outside the system, at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin was then solidified by cooling

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and cut with a strand cutter to obtain resin chips.
The resulting resin had a relative viscosity (RV) of
2.2 and a Co-b value of 7.9. The residual amounts of
phosphorous atoms and sodium atoms were P = 9 ppm
and Na = 10 ppm, respectively. The resulting resin
was dried in a 100 L blender at an inner temperature
of 120°C for 12 hours, and then cooled to obtain
chips. The RV was 2.25, the Co-b value was 9.9, and
the water content was 250 ppm, in this stage. The
polyamide resin composition was fused by using a
uniaxial extruder and extruded in a given amount at
a rate of 3 g/min by using a gear pump. Foreign
matters in the polymer were filtered with a filter
having a filtering diameter of 20 μm, and the
pressure on the secondary side of the gear pump was
recorded with lapse of time. The back pressure
increasing coefficient K* after extruding for 4
hours was 3.8. Observation of the filter revealed
that no clogging was found. Observation of the heat
deterioration state of the resulting extrusion
molded article revealed that no gelled product due
to heat deterioration was observed.

[0077]

EXAMPLE B-7

In a preparation vessel having an inner capacity of 250 L equipped with an agitator, a partial condenser, a thermometer, a dropping funnel and a nitrogen gas introducing tube, 27.66 kg of m-xylylenediamine, 26.41 kg of adipic acid and 3.45 kg of cyclohexanedicarboxylic acid, which had been precisely weighed, were mixed at an inter temperature of 100°C to obtain a transparent solution. 1.54 g of $NaH_2PO_2 \cdot H_2O$ and 0.8 g of CH_3COONa as additives were added thereto, followed by agitating for 15 minutes. The resulting solution was transferred to a reaction vessel having an inner capacity of 270 L, and then reacted under stirring in conditions of an inner temperature of 190°C and an inner pressure of 1.0 MPa. While water distilled was removed outside the system, at a time where the inner temperature became 235°C, the inner pressure was returned to ordinary pressure over 60 minutes. The inner temperature was gradually increased to 260°C. The solution was agitated at ordinary pressure, and the stirring operation was terminated when a target viscosity was obtained, followed by allowing to stand for 20 minutes. Thereafter, a molten resin was taken out from a discharge port at a lower part of the reaction vessel, and the resin

was then solidified by cooling and cut with a strand
cutter to obtain resin chips. The resulting resin
had a relative viscosity (RV) of 2.3 and a Co-b
value of 6.6. The residual amounts of phosphorous
atoms and sodium atoms were P = 9 ppm and Na = 10
ppm, respectively. The resulting resin was dried in
a 100 L blender at an inner temperature of 120°C for
12 hours, and then cooled to obtain chips. The RV
was 2.30, the Co-b value was 6.9, and the water
content was 250 ppm, in this stage. The polyamide
resin composition was fused by using a uniaxial
extruder and extruded in a given amount at a rate of
6 g/min by using a gear pump. Foreign matters in the
polymer were filtered with a filter having a
filtering diameter of 20 μm, and the pressure on the
secondary side of the gear pump was recorded with
lapse of time. The back pressure increasing
coefficient K* after extruding for 4 hours was 2.8.
Observation of the filter revealed that no clogging
was found. Observation of the heat deterioration
state of the resulting extrusion molded article
revealed that no gelled product due to heat
deterioration was observed.

[0078]

EXAMPLE B-8

The polymerization method of polyamide was carried out in the same manner as in Example B-1 except that 0.53 g of H_3PO_2 and 1.5 g of $LiOH \cdot H_2O$ as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 9.2. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.67, the Co-b value was 9.4, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 5 ppm, Na = 0.1 ppm and Li = 5 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 2.2. Observation of the filter revealed that no clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no

gelled product due to heat deterioration was
observed.

[0079]

EXAMPLE B-9

The polymerization method of polyamide was
carried out in the same manner as in Example B-1
except that 0.53 g of H_3PO_2 and 0.8 g of KOH as
additives were added. The resulting resin had a
relative viscosity (RV) of 2.10 and a Co-b value of
8.9. The resulting resin was dried in a 100 L
blender at an inner temperature of 120°C for 12 hours,
further subjected to solid phase polymerization at
an inner temperature of 180°C, and then cooled to
obtain chips. The RV was 2.62, the Co-b value was
9.2, and the water content was 200 ppm, in this
stage. The residual amounts of phosphorous atoms and
sodium atoms were P = 5 ppm, Na = 0.1 ppm and K = 5
ppm, respectively. The polyamide resin composition
was fused by using a uniaxial extruder and extruded
in a given amount at a rate of 3 g/min by using a
gear pump. Foreign matters in the polymer were
filtered with a filter having a filtering diameter
of 20 μm, and the pressure on the secondary side of
the gear pump was recorded with lapse of time. The
back pressure increasing coefficient K* after

extruding for 4 hours was 3.8. Observation of the

filter revealed that no clogging was found.

Observation of the heat deterioration state of the

resulting extrusion molded article revealed that no

gelled product due to heat deterioration was

observed.

[0080]

REFERENCE EXAMPLE 1

The polymerization method of polyamide was

carried out in the same manner as in Example A-1

except that 0.86 g of $NaH_2PO_2 \cdot H_2O$ and 2.65 g of

CH_3COONa as additives were added. The resulting

resin had a relative viscosity (RV) of 2.11 and a

Co-b value of 5.0. The resulting resin was dried in

a 100 L blender at an inner temperature of 120°C for

12 hours, and then cooled to obtain chips. The chips

had a water content of 250 ppm. The residual amounts

of phosphorous atoms and sodium atoms were P = 25

ppm and Na = 93 ppm, respectively. The polyamide

resin composition was fused by using a uniaxial

extruder and extruded in a given amount at a rate of

6 g/min by using a gear pump. Foreign matters in the

polymer were filtered with a filter having a

filtering diameter of 20 μm, and the pressure on the

secondary side of the gear pump was recorded with

lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 4.5. Observation of the filter revealed that clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that no gelled product due to heat deterioration was observed.

[0081]

REFERENCE EXAMPLE 2

The polymerization method of polyamide was carried out in the same manner as in Example 1 except that 5.1 g of $NaH_2PO_2 \cdot H_2O$ and 4.0 g of CH_3COONa as additives were added. The resulting resin had a relative viscosity (RV) of 2.15 and a Co-b value of 3.4. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was 3.8, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 30 ppm and Na = 45 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear

pump. Foreign matters in the polymer were filtered
with a filter having a filtering diameter of 20 μm,
and the pressure on the secondary side of the gear
pump was recorded with lapse of time. The back
pressure increasing coefficient K* after extruding
for 4 hours was 6.0. Observation of the filter
revealed that slight clogging was found but was in a
level causing no practical problem. Observation of
the heat deterioration state of the resulting
extrusion molded article revealed that no gelled
product due to heat deterioration was observed.

[0082]

COMPARATIVE EXAMPLE 1

The polymerization method of polyamide was
carried out in the same manner as in Example A-1
except that 6.84 g of $NaH_2PO_2 \cdot H_2O$ and 10.59 g of
CH_3COONa as additives were added. The resulting
resin had a relative viscosity (RV) of 2.15 and a
Co-b value of -2.2. The resulting resin was dried in
a 100 L blender at an inner temperature of 120°C for
12 hours, further subjected to solid phase
polymerization at an inner temperature of 180°C, and
then cooled to obtain chips. The RV was 2.65, the
Co-b value was -2.9, and the water content was 200
ppm, in this stage. The residual amounts of

phosphorous atoms and sodium atoms were P = 200 ppm
and Na = 440 ppm, respectively. The polyamide resin
composition was fused by using a uniaxial extruder
and extruded in a given amount at a rate of 3 g/min
by using a gear pump. Foreign matters in the polymer
were filtered with a filter having a filtering
diameter of 20 μm, and the pressure on the secondary
side of the gear pump was recorded with lapse of
time. The back pressure increasing coefficient K*
after extruding for 4 hours was 20. Observation of
the filter revealed that clogging was found.
Observation of the heat deterioration state of the
resulting extrusion molded article revealed that no
gelled product due to heat deterioration was
observed.

[0083]

COMPARATIVE EXAMPLE 2

The polymerization method of polyamide was
carried out in the same manner as in Example A-1
except that 4.55 g of $NaH_2PO_2 \cdot H_2O$ and 3.52 g of
CH_3COONa as additives were added. The resulting
resin had a relative viscosity (RV) of 2.15 and a
Co-b value of -1.0. The resulting resin was dried in
a 100 L blender at an inner temperature of 120°C for
12 hours, further subjected to solid phase

polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was -1.7, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 133 ppm and Na = 190 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 29. Observation of the filter revealed that clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that gelled products due to heat deterioration were observed.

[0084]

COMPARATIVE EXAMPLE 3

The polymerization method of polyamide was carried out in the same manner as in Example A-1 except that 5.13 g of $NaH_2PO_2 \cdot H_2O$ and 3.42 g of CH_3COONa as additives were added. The resulting

resin had a relative viscosity (RV) of 2.15 and a Co-b value of -1.0. The resulting resin was dried in a 100 L blender at an inner temperature of 120°C for 12 hours, further subjected to solid phase polymerization at an inner temperature of 180°C, and then cooled to obtain chips. The RV was 2.65, the Co-b value was -1.5, and the water content was 200 ppm, in this stage. The residual amounts of phosphorous atoms and sodium atoms were P = 100 ppm and Na = 220 ppm, respectively. The polyamide resin composition was fused by using a uniaxial extruder and extruded in a given amount at a rate of 3 g/min by using a gear pump. Foreign matters in the polymer were filtered with a filter having a filtering diameter of 20 μm, and the pressure on the secondary side of the gear pump was recorded with lapse of time. The back pressure increasing coefficient K* after extruding for 4 hours was 17. Observation of the filter revealed that clogging was found. Observation of the heat deterioration state of the resulting extrusion molded article revealed that gelled products due to heat deterioration were observed.

[0085]

TABLE 1

	Dicarboxylic acid/diamine (mol%)	P atom (ppm)	Alkali metal atom (M)		M/P molar ratio	RV	Color b	Back pressure increasing coefficient K*	Filter clogging	State of heat deterioration
			Species	(ppm)						
Example a-1	AA//MXDA 100//100	40	Na	4.5	4.5	2.10	3.3	2.5	AA	A
Example a-2	AA//MXDA 100//100	50	Na	4.0	4.0	2.23	3.1	3.5	AA	A
Example a-3	AA//MXDA 100//100	100	Na	3.5	3.5	2.65	-1.1	14	A	A
Example a-4	AA//MXDA 100//100	100	Na	4.0	4.0	2.65	-1.3	7.8	A	A
Example a-5	AA//MXDA 100//100	100	Na	5.0	5.0	2.12	1.0	3.7	AA	A
Example a-6	AA//MXDA 100//100	100	Na	5.0	5.0	2.65	2.0	4.5	AA	A
Example a-7	AA//MXDA 100//100	150	Na	5.0	5.0	2.50	1.5	5.2	A	A
Example a-8	AA//MXDA 100//100	190	Na	6.0	6.0	2.1	2.5	4.0	AA	A
Example a-9	AA/TPA/MXDA 90/10/100	150	Na	4.5	4.5	2.35	4.9	14	A	A
Example a-10	AA/CHDA/MXDA 90/10/100	150	Na	4.5	4.5	2.30	-2.3	12	A	A
Example b-1	AA//MXDA 100//100	1	Na	1	-	2.65	6.5	3.0	AA	A
Example b-2	AA//MXDA 100//100	0	Na	0.1	-	2.65	7.8	2.2	AA	A
Example b-3	AA//MXDA 100//100	5	Na	5	-	2.65	6.2	3.9	AA	A

(continued)

TABLE 1

	Dicarboxylic acid/diamine (mol%)	P atom (ppm)	Alkali metal atom (M) Species	(ppm)	M/P molar ratio	RV	Color b	Back pressure increasing coefficient K*	Filter clogging	State of heat deterioration
Example b-4	AA//MXDA 100//100	9	Na	9	–	2.15	5.3	4.6	AA	A
Example b-5	AA//MXDA 100//100	15	Na	15	–	2.65	3.6	4.5	AA	A
Example b-6	AA/TPA/MXDA 90/10/100	9	Na	10	–	2.25	9.9	3.8	AA	A
Example b-7	AA/CHDA/MXDA 90/10/100	9	Na	10	–	2.30	6.9	2.8	AA	A
Example b-8	AA//MXDA 100//100	5	Li Na	5 0.1	–	2.67	9.4	2.2	AA	A
Example b-9	AA/TPA/MXDA 90/10/100	5	K Na	5 0.1	–	2.62	9.2	3.8	AA	A
Reference example 1	AA//MXDA 100//100	25	Na	93	5.0	2.11	5.0	4.5	AA	A
Reference example 2	AA//MXDA 100//100	30	Na	45	–	2.65	3.8	6.0	A	A
Comparative example 1	AA//MXDA 100//100	200	Na	3.0	3.0	2.65	-2.9	20	B	A
Comparative example 2	AA//MXDA 100//100	133	Na	2.0	2.0	2.61	-1.7	29	B	B
Comparative example 3	AA//MXDA 100//100	100	Na	3.0	3.0	2.65	-1.5	17	B	B

[0086]

NOTE

AA: adipic acid

TPA: terephthalic acid

CHDA: 1,4-cyclohexanedicarboxylic acid

MXDA: m-xylylenediamine

The Co-b values were those after drying and solid

phase polymerization.

Filter clogging

AA: No clogging was found.

A: Slight clogging was found but was in a level

causing no practical problem.

B: Clogging was found.

State of heat deterioration

A: No gelled product was found.

B: Gelled products were found.

INDUSTRIAL APPLICABILITY

[0087]

The polyamide resin composition of the invention is

good in heat stability upon molding, is excellent in color

tone, and suffers less increase in filter back pressure.

The invention is suitably used as a material of a gasoline tank and a material of a molded article, such as a hollow molded container including a beverage bottle, a film and a sheet, and can produce them with high productivity.